

# **Electron Emission from Diamondoids: a DMC Study**

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## Semiconductor Nanoparticles for Optoelectronic Devices (I)

- The *optical gap* (OG) is the difference between the ground-state and first-excited-state energies of a molecule.
- *Quantum-confinement* (QC) effects should elevate the OGs of nanoparticles of group-IV elements above the corresponding bulk band gaps.
- The effect is caused by the increase in the KE of a state when it is spatially confined.

## Semiconductor Nanoparticles for Optoelectronic Devices (II)

- Films of nanoparticles can be placed on the surfaces of photodiodes and LEDs.
- Si and Ge nanoparticles have been studied extensively, as they can be integrated with existing device fabrication techniques.
- Until recently, carbon nanoparticles have been more difficult to synthesise and study.
- The diamond band gap (5.47 eV) is in the UV range.
- QC might push the OGs of carbon nanoparticles even further into the UV range, allowing UV sensors to respond to higher frequencies than ever before.

## Semiconductor Nanoparticles for Electron-Emission Devices (I)

- The electron affinity (EA) of a molecule is the energy released when the molecule and a free electron form an ion.
- The EA of a semiconductor or insulator is the difference between the conduction-band minimum and the vacuum level.
- Some hydrogen-terminated diamond surfaces have negative EAs.
- So hydrogen-terminated carbon nanoparticles should have low or negative EAs.

## Semiconductor Nanoparticles for Electron-Emission Devices (II)

- Conventional TV tubes involve heating a metal element to produce electrons, accelerating them down a vacuum tube using an electric field, and moving the resulting beam across a phosphor screen using magnetic fields.
- Would like to have a large, light, flat, power-efficient display device that doesn't have the limitations of LCD screens (e.g., slow response time, limited viewing angle).
- Idea: develop *field emission devices*, in which each pixel has its own cold electron-emitter, with the electrons being pulled off the emitter by an electric field.

## **Semiconductor Nanoparticles for Electron-Emission Devices (III)**

- The strength of electric field required is most serious problem with this technology.
- Materials with negative electron affinities will readily emit conduction electrons.
- Hence the electric field required to pull the electrons off such materials would not need to be especially strong.

## Diamondoids

- Hydrogen-terminated carbon nanoparticles are called *diamondoids*.
- Chemists from ChevronTexaco have isolated diamondoids from petroleum.
- Crystals of diamondoids have been grown.
- Functional groups have been added to diamondoids.
- Polymers of diamondoids with up to  $10^6$  repeat units have been produced.

## Experimental Results

- An XANES study found substantial QC in diamondoids of up to several nanometres in diameter.
- A NEXAFS study found no evidence of QC in such nanoparticles.
- No experimental studies of electron affinities of carbon nanoparticles?
- Several technologically important questions, but the experimental results are contradictory or nonexistent.
- Accurate first-principles simulations are clearly required!



## Previous DFT Simulations

- DFT OGS are always underestimated: this is the well-known “band-gap” problem.
- One DFT study predicted that the OGS of diamondoids fall off rapidly as their diameter increases.
- At 1 nm, the OGS were predicted to lie below the band gap of diamond.
- Another DFT study found that the OGS of the same molecules are substantially higher than the diamond gap.
- No DFT results for electron affinity?
- More accuracy required? Use QMC!

## The QMC Calculations (I)

- C and H pseudopotentials were used.
- The Troullier-Martins C psps from the ABINIT web site give smaller variances and more stable DMC than the Hamann ones.
- Very large boxes (side-length 35–50 a.u.) and plane-wave cutoff energies (35–50 Ry) were used for the DFT calculations.
- Orbitals were represented by splines on a grid in real space.
- The time step was 0.02 a.u.; the resulting errors are negligible.

## The QMC Calculations (II)

- Changing the XC functional used to generate nanoparticle geometry and trial wave function altered the DMC OG by 0.3 eV.
- The HOMO was replaced by the LUMO in the spin-down Slater determinant to give the excited-state wave function.
- Typically, this introduces an error of 0.1–0.2 eV into the excited-state DMC energy.
- Overall, the error in the DMC OG is expected to be about 0.5 eV.

## Optical-Gap Results

- The DFT OGs are lower than the DMC gaps by about 2 eV.
- The DMC OG decreases rapidly with cluster size, falling below the bulk gap at a size of about 1 nm in diameter.
- Not quite what was hoped for!
- Differs from the behaviour of the OG in Si and Ge nanoparticles.
- DFT is qualitatively (not quantitatively) correct in all cases.
- Why does the QC model apply to Si and Ge nanoparticles, but not carbon ones?

## Nature of the HOMO and LUMO for Diamondoids (I)

- The HOMO is located on the atoms and bonds within the nanoparticle.
- LUMO is a diffuse surface state for diamondoids; this not the case for Si or Ge.
- The HOMO evolves into the valence-band maximum as the cluster size increases.
- The LUMO does **not** evolve into the conduction-band minimum. It is like a surface or impurity state within the band gap.
- The LUMO is clearly not confined.

## Nature of the HOMO and LUMO for Diamondoids (II)

- The LUMO is essentially unbound; this suggests EA will be small or negative.
- The disagreement between previous DFT results arose because one group used an inadequate Gaussian basis set to describe the diffuse LUMO. The LUMO was therefore artificially localised, producing a spurious QC effect.

## Electron Affinities of Diamondoids

- DFT and DMC electron affinities and ionisation potentials are in close agreement.
- The electron affinities are negative, as was hoped.
- Diamondoids are therefore candidates for use as low-voltage electron emitters.
- Other candidates exist. Whether diamondoids turn out to be the best option depends on how cheaply and easily they can be produced.

## Future Work

- I'd like to study the effect of adding hydroxyl and carboxyl groups to diamondoids.
- I'd like to study polymers of functionalised diamondoids.
- Is the LUMO still delocalised? What happens to the OGS and electron affinities? What are the elastic properties of diamondoid polymers?
- *Buckydiamonds* are recently discovered carbon molecules with diamond-like interiors and fullerene-like exteriors.
- I hope to explore the optical and chemical properties of these new materials.